

April 2017

STUDY OF CSSNBR3

Weiran Gao
Worcester Polytechnic Institute

Follow this and additional works at: <https://digitalcommons.wpi.edu/mqp-all>

Repository Citation

Gao, W. (2017). *STUDY OF CSSNBR3*. Retrieved from <https://digitalcommons.wpi.edu/mqp-all/4103>

This Unrestricted is brought to you for free and open access by the Major Qualifying Projects at Digital WPI. It has been accepted for inclusion in Major Qualifying Projects (All Years) by an authorized administrator of Digital WPI. For more information, please contact digitalwpi@wpi.edu.

Synthesis and quantification of interfacial Br^- basicity on CsSnBr_3



WPI

A Major Qualifying Project Report
Submitted to the Faculty of the
WORCESTER POLYTECHNIC INSTITUTE
in partial fulfillment of the requirements for the
Degree of Bachelor of Science

By:
Weiran Gao

Date: April 27, 2017

Approved:

Professor Ronald L. Grimm, Primary Advisor

This report represents the work of WPI undergraduate students submitted to the faculty as evidence of completion of a degree requirement. WPI routinely publishes these reports on its website without editorial or peer review. For more information about the projects program at WPI, please see
<http://www.wpi.edu/academics/ugradstudies/project-learning.html>

Abstract

We synthesized cesium tin bromide (CsSnBr_3), a solar energy conversion material with a band gap of 1.7 eV, using both solution cooling method and high temperature melt method. X-ray photoelectron spectroscopy (XPS) and powder X-ray diffraction characterized the synthesized crystals. We studied the basicity of interfacial Br^- sites on CsSnBr_3 by reacting the synthesized crystals with boron trifluoride (BF_3) and tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$). XPS data give F 1s to Br 3d peak area ratios of 0.69 and 0.80 for BF_3 and $\text{B}(\text{C}_6\text{F}_5)_3$ treated CsSnBr_3 , respectively. These correspond to surface coverages of 190% for BF_3 45% for $\text{B}(\text{C}_6\text{F}_5)_3$. We interpreted the desorption temperature of the BF_3 treated sample to be 230 °C from temperature programmed desorption (TPD) data, which implies a boron- bromine bond strength of 132 kJ/ mol.

1. Introduction

Studies on perovskite materials such as methylammonium lead iodide have been booming during the past few years because perovskite materials are inexpensive and can potentially achieve high solar energy conversion efficiency. However, the instabilities of these materials limit their long-term applications, and studies regarding the interfacial chemical states are required in order to passivate the material surfaces.

In this study, we are particularly interested in exploring the interfacial Br⁻ basicity on cesium tin bromide (CsSnBr₃). CsSnBr₃ is a lead-free perovskite material with an experimentally obtained band gap of 1.7 eV [1]. The material is sensitive to air because Sn^{II} in the structure has the tendency to be oxidized to Sn^{IV}. As is shown in Figure 1, the surface of CsSnBr₃ is full of Br⁻ sites that can provide Lewis basicity. In this study, we hypothesize that these interfacial Br⁻ sites will react with Lewis acids. By understanding the basicity of the interfacial Br⁻ sites, we will have the ability to passivate the surfaces using techniques such as atomic layer deposition (ALD), which will ultimately lead to fabrications of more efficient photovoltaic devices.

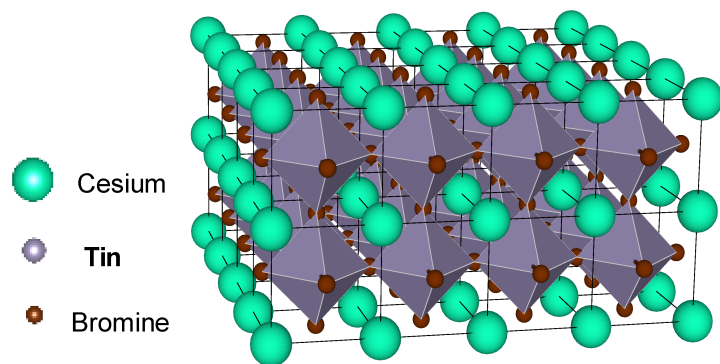


Figure 1. This is text. I want to see where the second line is going to go.

This study contains two parts. The first part is to synthesize CsSnBr₃ crystals, which was achieved by two methods: solution cooling method and furnace melting method. This was followed by characterization of the crystals. The second part details our study of the Lewis basicity of the interfacial Br⁻ species. Both boron trifluoride and tris(pentafluorophenyl)borane were used to react with CsSnBr₃ crystals. X-ray

photoelectron spectroscopy (XPS) quantified interfacial oxidation states and fractional coverage of surface-adsorbed species while temperature programmed desorption (TPD) quantified the strength of interactions between the BF_3 adsorbate and the CsSnBr_3 substrate.

2. Experimental Section

2.1. *Synthesis of CsSnBr_3*

2.1.1. Chemicals

Cesium bromide (CsBr), tin bromide (SnBr_2), boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$), tris(pentafluorophenyl)borane were used as obtained. Dichloromethane and hexanes were stored over 3 Å molecular sieves prior to use. Ethylene glycol was degassed and stored in a glovebox prior to use.

2.1.2. Solution synthesis of CsSnBr_3

A 0.4 M solution of cesium bromide and tin bromide was made in ethylene glycol. The solution was held at 130 °C to allow the precursors to dissolve. The temperature was then ramped down to 68 °C over the course of 13 days. Millimeter-sized cubic black shiny crystals formed during the process (Fig. 2a). The experiment was conducted in an argon-filled glovebag.

2.1.3. Furnace synthesis of CsSnBr_3

A 1:1 ratio of cesium bromide and tin bromide was added to a quartz tube. The tube was flame-sealed under vacuum to exclude O_2 , and then placed in a furnace and heated to 620 °C. The temperature was held at 620 °C for 8 hrs, then ramped down to 370 °C over 4 days. After cooling down to ambient temperature, the tube was broken in an argon-filled glovebag to isolate the shiny black ingot CsSnBr_3 that was formed from the reaction (Fig. 2b).

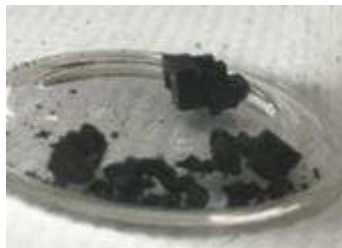


Figure 2. (a) Crystals grown from solution method. The largest crystal is 0.3 cm tall and 0.7 cm wide.



(b) Crystals grown from furnace method. The largest crystal is 1 cm wide by 1.5 cm tall.

2.2. Surface reactions

2.2.1. Boron trifluoride adsorption

A 0.1 M solution of boron trifluoride was made using $\text{BF}_3 \cdot \text{OEt}_2$ in a 10:1 mixture of hexane and dichloromethane. The solution was used to react with CsSnBr_3 crystals made from furnace method for 10 minutes at 45 °C under argon. After removal of the solution, the crystals were triple rinsed with the solvent to remove any physisorbed species. The crystals were then dried under vacuum and stored in an argon-filled glovebox for future characterization.

2.2.2. Tris(pentafluorophenyl)borane adsorption

CsSnBr_3 was reacted with 0.1 M solution of tris(pentafluorophenyl)borane in 10:1 mixture of hexane and dichloromethane using the same method as described above.

2.3. Powder X-ray diffraction (XRD)

Powder XRD data of CsSnBr_3 crystals were collected using a Bruker-AXS D8 focus powder X-ray diffractometer with $\text{Cu-K}\alpha_1$ radiation in the range of 10–50° (2 θ) with a step size of 0.05° and 2 s. The running conditions for the X-ray tube were 40 kV and 40 mA. The CsSnBr_3 crystals obtained from the furnace method were ground into a black powder using a mortar in an argon-filled glovebox. The sample was covered using Low-Static Kapton Tape during the XRD process to avoid contact with O_2 . Powder XRD data of CsBr_3 and SnBr_2 powders were collected using the same instrumental settings.

2.4. X-ray Photoelectron Spectroscopy (XPS)

2.4.1. Instrumentation

XPS characterized the CsSnBr₃ crystals made from the furnace method as well as to determine the surface layer coverages of boron trifluoride and tris(pentafluorophenyl)borane on CsSnBr₃. The instrumentation used was a Perkin Elmer PHI5600 with a monochromatized K_α aluminium x-ray source. The pass energy was 23.5 eV with a step size of 25 meV and a dwell time setting of 50 ms per step.

2.4.2. Data Interpretation

Surface layer coverages were calculated using the equations relating the relative intensities and attenuation lengths along with the physical characteristics of the sample.

$$I_{F\ 1s}(d) = SF_{F\ 1s} \rho_F \lambda_{F\ 1s} \cos \theta \left[1 - \exp \left(\frac{-d}{\lambda_{F\ 1s} \cos \theta} \right) \right] \quad (1)$$

$$I_{Br\ 3d}(d) = SF_{Br\ 3d} \rho_{Br} \lambda_{Br\ 3d} \exp \left(\frac{d}{\lambda_{Br\ 3d} \cos \theta} \right) \quad (2)$$

In eq 1 and 2, I_{F1s} and I_{Br3d} are the signal intensities determined from the XPS data. Terms $SF_{F1s} = 1.000$ and $SF_{Br3d} = 0.895$ represent the fluorine and bromine atomic sensitivity factors that are provided by the manufacturer [2].

The term θ is the angle to the detector from the sample (45° in this case). The term d refers to the integral across the area of material that is coating the substrate. The attenuation lengths $\lambda_{F\ 1s} = 2.5$ nm and $\lambda_{Br\ 3d} = 2.16$ nm are calculated for the materials using the equation:

$$\lambda = 0.41a^{3/2}E^{1/2} \quad (3)$$

where a is the atomic diameter for the atom of interest, and E is the kinetic energy of electrons observed. The terms ρ_F and ρ_{Br} denote the volume densities of fluorine and bromine atoms, respectively. The value of ρ_{Br} is 15.3 based on 3 atoms occupying a unit cell of 0.196 nm³. Getting ρ_F from solving eq 4, which represents the experimentally determined ratio of I_{F1s}/I_{Br3d} with $d = 0.214$ nm, or the height of the BF₃ moiety on the CsSnBr₃ surface.

$$\frac{I_{F1s}}{I_{Br3d}} = \frac{SF_{F1s}}{SF_{Br3d}} \frac{\rho_F}{\rho_{Br}} \frac{\lambda_{F1s} \cos \theta}{\lambda_{Br3d}} \left[1 - \exp\left(\frac{-0.214 \text{ nm}}{\lambda_{F1s} \cos 45^\circ}\right) \right] \exp\left(\frac{0.214 \text{ nm}}{\lambda_{Br3d} \cos 45^\circ}\right) \quad (4)$$

Based on the calculated value of ρ_F , X-ray photoelectron spectroscopy (XPS) one obtains coverages based on the same thickness d and convert them to fractional coverage based on an Br site density of 2.97 sites per nm² based on the CsSnBr₃ unit cell dimensions [3].

2.5. Temperature Programmed Desorption (TPD)

2.5.1. Instrumentation

TPD determined the bond strengths between surface-adsorbed boron and the substrate-bound bromide. The sample was heated up under UHV conditions to approximately 400 °C with a constant heating rate of 0.25 K s⁻¹. The mass spectrometer used to analyze the gas in the chamber was an RGA 200 (SRS, Sunnyvale, California).

2.5.2. Interpretation of desorption spectra

Br-B bond strength was calculated from TPD data using the equation:

$$\frac{dN}{dT} = AN^n \beta^{-1} \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

where A is the attempt frequency, which is the frequency of bond stretching between the substrate and adsorbate, and is typically taken as 10¹³ s⁻¹. N is the surface coverage in molecules, and the superscript n denotes the desorption order. In this case, the desorption is assumed to be first order. β is the heating rate, which is 0.25 K s⁻¹ in this case. R is the gas constant, and T is the temperature in Kelvin. E_a is the desorption energy to be found by fitting the model over experimental data.

3. Results

3.1. *CsSnBr₃ bulk crystals synthesis*

The XPS and powder XRD in Fig. 4 demonstrated that CsSnBr₃ crystals were successfully grown from the high temperature melting method. Photoelectron spectra demonstrate trace amounts of oxidized Sn^{IV} and no detectable O 1s feature below 530 eV that would be attributed to deleterious oxidation of metal species (i.e. CsO_x, SnO_x).

The powder XRD signal of the synthesized material is in agreement with literature values for CsSnBr₃[4].

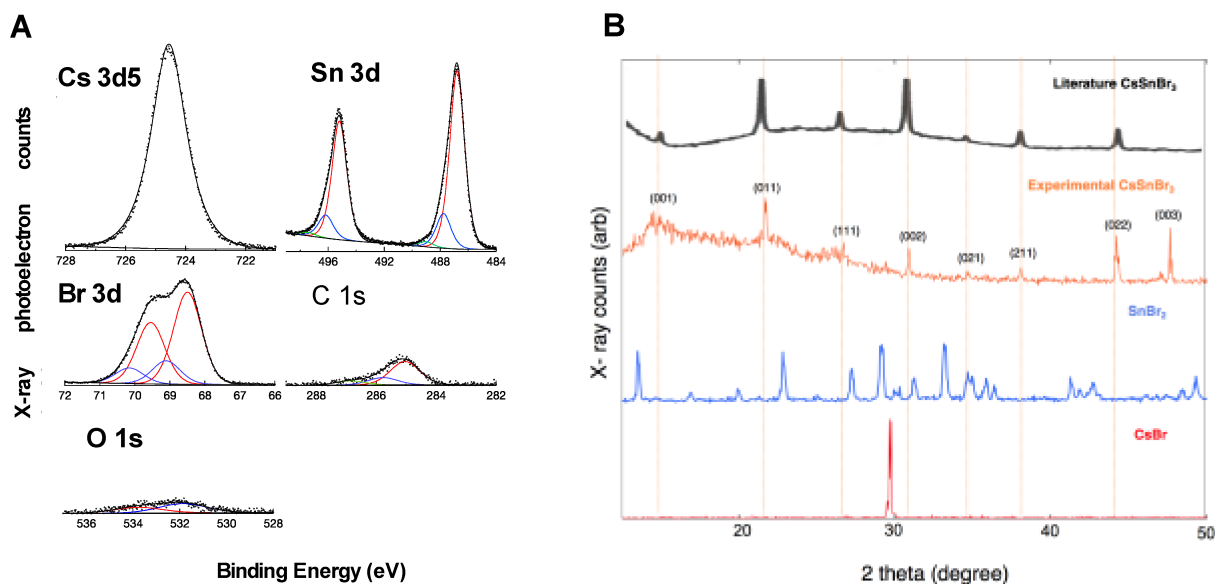


Figure 3. XPS (A) and powder XRD (B) of CsSnBr₃ synthesized from a high-temperature melt.

3.2. Boron Trifluoride Adsorption

3.2.1. XPS analysis

XPS data of CsSnBr₃ after BF₃ exposure are shown in Fig. 4. The relatively strong feature in the F 1s region implies successful adsorption of BF₃ molecules onto CsSnBr₃ surface. The B 1s feature is not able to be analyzed because it is in the same region as Br 3p but with a much smaller sensitivity factor. The peak areas and calculated BF₃ coverage are shown in Table 1.

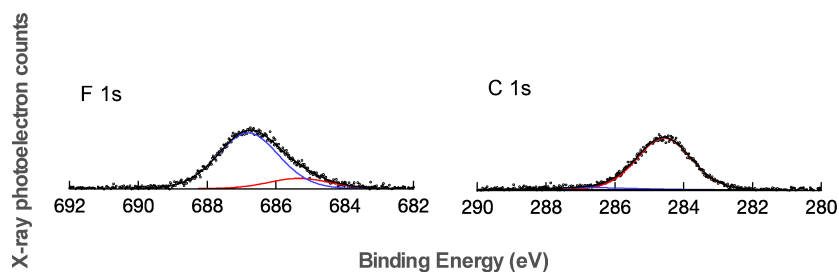


Figure 4. XPS of CsSnBr₃ after reacting with BF₃ for 10 minutes.

Br 3d Area	F 1s Area	Coverage (%)
1609.7	1118.7	190 \pm 10

Table 1. Peak areas and calculated BF₃ coverage for CsSnBr₃. Area units are cps eV.

3.2.2. *TPD analysis*

TPD data of the BF₃⁻ treated CsSnBr₃ sample are shown in Fig. 6. Based on the mass spectrum of boron trifluoride [5], major fragmentation signals can be detected at mass to charge ratios of 48 and 49, which correspond to BF₂⁺ with ¹⁰B and ¹¹B isotopes. The signal intensities at 48 m/z and 49 m/z should have a ratio of 1:3. The signal at 50 m/z was also examined as a control signal since there should be no significant signal detected. In Fig. 6, the signal intensity ratio of 49m/z to 48 m/z is approximately 1:3, which agrees with the BF₃ mass spectrum. No significant signals were detected at 50m/z, which also provides evidence that BF₃ is desorbing from the surface. However, the peak shapes are not to be expected in a typical desorption process. We theorized the following to help explain the data:

- (1) The desorption process started at about 230 °C. We plotted a model with a peak temperature of 230 °C to fit the data, which is shown in the figure as pink lines. The fitted model has a 1:3 intensity ratio for 48 m/z and 49 m/z corresponding to the BF₃ mass spectrum. As the figure shows, the model fits the data trend around 230 °C fairly well, indicating that the model is a proper representation of the desorption process.
- (2) The data start to show dramatic peaks at around 250 °C. We believe this is an artifact possibly due to inaccurate readings of thermocouples. One evidence is that the CsSnBr₃ sample has already melted when the highest temperature given by the thermocouples is about 400 °C, while the literature-reported melting point for CsSnBr₃ is about 450 °C [6].

- (3) The peaks after 300 °C are possibly due to crystal melting, at which point all the adsorbed BF_3 are released from the crystal.

With a peak temperature of 230 °C, the fitted model gives a desorption energy of 132 kJ/mol, which corresponds to the bond strength between the adsorbed boron species and the interfacial bromine sites.

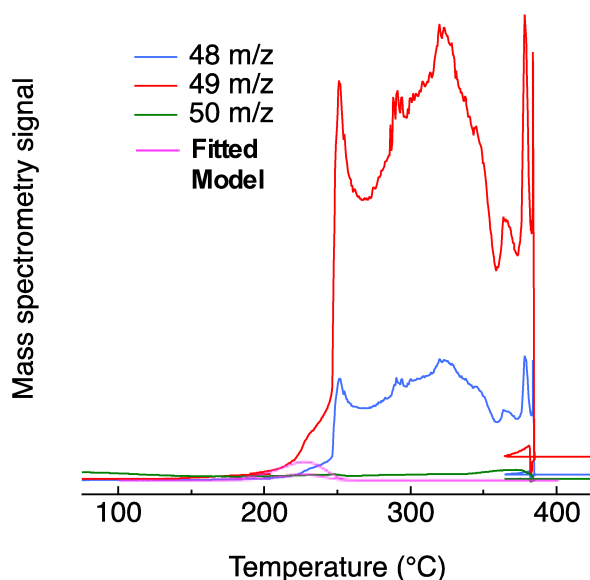


Figure 5. following a 10 minute exposure to BF_3 , TPD spectra at a heating rate of 2.5 K s^{-1} .

3.3. *Tris(pentafluorophenyl)borane Adsorption*

3.3.1. XPS analysis

XPS data of CsSnBr_3 after tris(pentafluorophenyl)borane exposure are shown in Fig. 6. The feature in the F 1s region indicates that tris(pentafluorophenyl)borane successfully reacted with the surface. The stronger feature in the C 1s region is possibly due to the carbon atoms in tris(pentafluorophenyl)borane, which also implies successful adsorption of the molecule. The calculated surface coverage is 45% (Table 2).

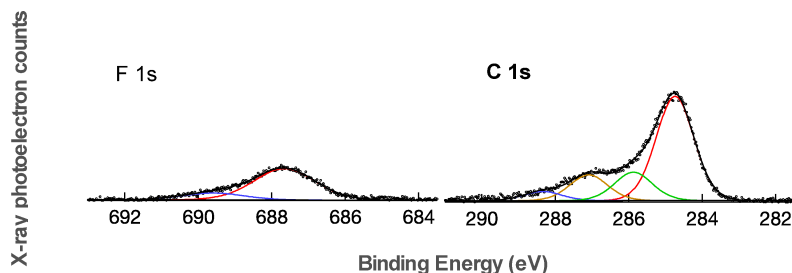


Figure 6. XPS of CsSnBr₃ after reacting with B(C₆F₅)₃ for 10 minutes.

Br 3d Area	F 1s Area	Coverage (%)
758.6	605.6	45 ± 5

Table 2. Peak areas and calculated B(C₆F₅)₃ coverage for CsSnBr₃. Area units are cps eV.

4. Discussion

Both BF₃ and B(C₆F₅)₃ demonstrate the abilities to adsorb on to CsSnBr₃ surfaces, which indicates that there are surface Br⁻ sites with Lewis basicity that is strong enough for these reactions to occur. The calculated BF₃ surface coverage is greater than 100%, which is possibly because during the calculation, the surface is assumed to be one uniform layer, whereas the CsSnBr₃ crystal used for the reaction is polycrystalline with observable surface defects. This means that the actual surface area of CsSnBr₃ crystal is likely to be much greater than the one used in the calculation. This leads to the next step of decreasing the surface defects using techniques such as polishing and chemical healing. Additionally, it is possible that because of the small volume of BF₃ molecules, each boron atom has multiple BF₃ molecules adsorbed. This would explain the high coverage since the calculations assume 1:1 ratio of boron-bromine adsorption. The calculated surface coverage of tris(pentafluorophenyl)borane is 45%, which is much smaller than that of BF₃. We attribute this decreased coverage to the fact that tris(pentafluorophenyl)borane molecules are fairly bulky, and thus the adsorbed

molecules have the ability to hinder other molecules from adsorbing onto the Br⁻ sites nearby.

The bond strength determined from TPD data suggested that the boron-bromine bonds are fairly strong. With a desorption energy of 132 kJ mol⁻¹, the adsorption of boron trifluoride on CsSnBr₃ surface can be classified as chemisorption [7]. This means that the Br⁻ sites are basic enough for strong Lewis acids like BF₃. We also acquired TPD data for the sample treated with tris(pentafluorophenyl)borane, but because there is no mass spectrum for this molecule, the TPD data are a general sweep at a broad range of mass to charge ratios, and need to be further analyzed.

5. Conclusions and Future work

5.1. Crystal growth and surface defect healing

We synthesized centimeter-sized polycrystalline CsSnBr₃ from a high temperature melt. The next step will be to synthesize CsSnBr₃ crystals with increased surface areas and decreased surface defects. One possible way to achieve this is to use the solution method with seed crystals. These seeds will act as nucleation sites and help increase the crystal size and reduce crystal amounts. Additionally, future work in this area will also include ways to refine the crystal surfaces to reduce structural defects. One possible way will be to reform grain boundaries and surfaces by exposing the crystals to methylamine gas, which was originally done on methylammonium lead iodide [8].

5.2. Lewis basicity study

This project studied the Lewis basicity of interfacial Br⁻ sites on CsSnBr₃ by reacting the crystals with strong Lewis acids such as boron trifluoride and tris(pentafluorophenyl)borane. Successful adsorptions of both molecules on CsSnBr₃ surfaces indicate that the interfacial Br⁻ sites are basic enough for such strong Lewis acids. The next step is to expand the study to probe the limit of this basicity. A series of Lewis acids with decreasing acidity shown in Fig. 7 will be used. All the fluorinated

Lewis acids except tris(pentafluorophenyl)borane studied in this project will be synthesized using Grignard reagents and air-free reaction techniques. Triphenylborane can be purchased and used as obtained. Reactions and the following adsorption analysis will be done in a similar fashion to the boron trifluoride study in this project. In a preliminary study, triphenylborane was used to react with CsSnBr_3 , although it is still not clear if the adsorption is successful because there is no fluorine atom in the molecule, and XPS cannot detect boron 1s directly due to the influence of Br 3p. In this case, TPD analysis will be used as the primary tool to determining successful adsorption.

The ultimate goal of this Lewis basicity study is to determine what types of precursors can be used for ALD surface passivation on CsSnBr_3 . There are hundreds of ALD precursor and oxidation strategy combinations, and we believe that understandings of surface reactivity of CsSnBr_3 will enable us to explore ALD passivation techniques in a strategic manner.

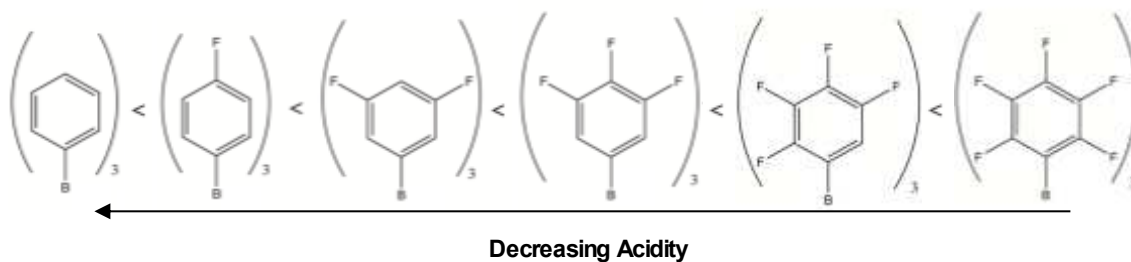


Figure 7. A series of Lewis acids to be used to Lewis basicity study of CsSnBr_3 .

6. References

1. Peedikakkandy, L., & Bhargava, P. (2016). Composition dependent optical, structural and photoluminescence characteristics of cesium tin halide perovskites. *RSC Adv.*, 6(24), 19857-19860. doi:10.1039/c5ra22317b
2. Briggs, D., Handbook of X-ray Photoelectron Spectroscopy C. D. Wanger, W. M. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg Perkin-Elmer Corp., Physical Electronics Division, Eden Prairie, Minnesota, USA, 1979. 190 pp. \$195. Surface and Interface Analysis, 1981. 3(4): p. v-v.
3. Huang, L., & Lambrecht, W. R. (2013). Electronic band structure, phonons, and exciton binding energies of halide perovskites CsSnCl₃, CsSnBr₃, and CsSnI₃. *Physical Review B*, 88(16). doi:10.1103/physrevb.88.165203
4. Sabba, D., Mulmudi, H. K., Prabhakar, R. R., Krishnamoorthy, T., Baikie, T., Boix, P. P., Mhaisalkar, S., & Mathews, N. (2015). Impact of Anionic Br-Substitution on Open Circuit Voltage in Lead Free Perovskite (CsSnI₃-xBr_x) Solar Cells. *The Journal of Physical Chemistry C*, 119(4), 1763-1767. doi:10.1021/jp5126624
5. NIST Mass Spec Data Center, S.E. Stein, director, "Mass Spectra" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, doi:10.18434/T4D303
6. Andrews, R. H., Donaldson, J. D., Silver, J., & White, E. A. (1975). Crystal growth of caesium tin(II) trichloro-bromides. *Journal of Materials Science*, 10(8), 1449-1451. doi:10.1007/bf00540836
7. . Lavrich, D. J., Wetterer, S. M., Bernasek, S. L., & Scoles, G. (1998). Physisorption and Chemisorption of Alkanethiols and Alkyl Sulfides on Au(111). *The Journal of Physical Chemistry B*, 102(18), 3456-3465. doi:10.1021/jp980047v
8. Zhou, Z., Wang, Z., Zhou, Y., Pang, S., Wang, D., Xu, H., Liu, Z., Padture, N. P. and Cui, G. (2015). Methylamine-Gas-Induced Defect-Healing Behavior of CH₃NH₃PbI₃Thin Films for Perovskite Solar Cells. *Angewandte Chemie*, 127(33), 9841-9845. doi:10.1002/ange.201504379